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PRODUCTION OF TITANIUM AND ZIRCONIUM BY REDUCTION OF THEIR SULFIDES

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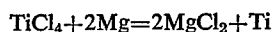
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The present invention relates to a method for producing titanium or zirconium metal and more particularly, to the production of titanium or zirconium metal by the reduction of the sulfides of these metals with an alkali metal to form elemental titanium or zirconium and as a by-product, the sulfides of the reducing agents.

Titanium and zirconium metals are growing in importance as articles of commerce. The unusual desirable properties of pure ductile titanium or zirconium, such as their high strength, and high corrosion resistance, make them ideal as structural materials, and consequently intensive searches are constantly being undertaken to develop improved and cheaper processes for their manufacture. In the following description only titanium is referred to in order to simplify the description, but it is understood that zirconium is also intended to be included.

At present, the titanium halides, and more particularly the chlorides, are generally accepted as the most economically feasible starting point for producing titanium metal. The reduction of titanium oxides is known to be very difficult. The chlorides are known to have higher bond energies than the corresponding iodides and accordingly the latter are more desirable for reduction purposes. However, the iodides are generally more expensive than the chlorides, and for this reason the latter are generally employed today as base materials for reduction. In the Kroll process, for example, molten magnesium metal and titanium tetrachloride, after purification by distillation, are charged into a reaction vessel, the titanium halide is reduced to titanium metal sponge, and as a byproduct the corresponding magnesium is formed:



In order to realize the elemental titanium, it is necessary to remove the magnesium chloride and any excess reducing agent. In one method the reaction product is leached with water or dilute acid and in another method it is subjected to a vacuum distillation, after the bulk of the molten magnesium chloride has been drained off. A better grade of titanium is obtained in the latter method which avoids aqueous leaching thereby freeing the mass of titanium sponge from the magnesium chloride without contamination by oxygen.

An impure metal can be produced if undistilled titanium tetrachloride is used, for example, and if the sponge is acid leached. But in this case, the metal obtained must then be purified, as by electro-refining. In these processes, the high cost of the tetrachloride and the stoichiometric requirement of the expensive reducing metal are serious disadvantages. When pure metal is produced vacuum evaporation of the residual reducing metal chloride contaminant is a slow process and furthermore requires a large expenditure for capital equipment. Aqueous acid leaching causes a significant oxide contamination, and/or objectionable hydride formation; as little as 0.1% to 1% of oxide contamination will cause an undesirable increase in hardness in the titanium metal produced, resulting in a low-grade product.

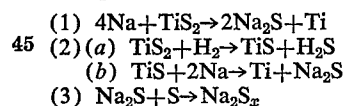
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It is the object of this invention to overcome the above and other disadvantages in present metallic reduction processes for producing titanium and/or zirconium. A specific object is to recover elemental high-grade titanium, substantially free of oxides, nitrides, and hydrides, from a reduction product without expensive decontamination methods known in the art. Another object is the production of a low cost impure titanium metal suitable for electro-refining.

This and other objects are achieved in this invention which broadly comprises reacting titanium sulfides including sulfides of di and trivalent titanium such as are represented by the formulas TiS , Ti_2S_3 , TiS_2 , with an alkali metal, preferably sodium or potassium at elevated temperatures, preferably between 800°C . and 1100°C ., in the presence of an inert or oxygen-free atmosphere such as argon, helium, etc., thereby forming elemental titanium with the sulfides of the reducing metal and possibly a small amount (excess) of the elemental reducing metal, the bulk of the molten alkali sulfide formed may be removed by draining. Upon cooling, to less than 500°C . and preferably to below 300°C . the removed alkali sulfide may be reacted with sulfur to form polysulfides which are then removed by draining. A final rinse with a non-aqueous solvent for the polysulfide leaves a high-grade metal without the necessity of vacuum distillation. Alternatively, the bulk, or the residual alkali sulfide (after drainage of the molten sulfide as above) may be leached with a non-aqueous solvent for the alkali sulfide.

The reduction of the titanium sulfide may be effected in a single step reduction with the alkali metal or a two-stage reduction, that is, in which the sulfide is in a first step partially reduced by heat decomposition and/or by hydrogen reduction at about 1100°C ., followed by a final step of the reduction with an alkali metal such as sodium or potassium.

In the process of this invention the reducing metals leading to elemental titanium include alkali metals such as sodium or potassium, and preferably the metal sodium. Hydrogen may be used to produce a sulfide of lower valence titanium from one of higher valence titanium at about 1100°C . The reactions may be represented, for example, as follows:



In the two-step reduction of titanium sulfide noted in (2) above, hydrogen (used in the first step) is a much cheaper reducing agent than the sodium used in the second step, and accordingly this method includes economies in the cost of the reducing agent usually employed. Also, since less sodium sulfide is formed, less sulfur would be required to form the low melting sodium polysulfide if the preliminary molten alkali sulfide draining is omitted.

The alkali sulfides present as byproducts with the metallic titanium may be economically removed by the addition of sulfur at elevated temperatures to form the polysulfides of the alkali metal and the latter drained away from the titanium at temperatures above the melting point of said polysulfides, namely, 275°C . The adhering remaining polysulfides and elemental sulfur are soluble in non-aqueous liquids and may accordingly be leached out of the reaction product without employing an aqueous solvent, the latter being undesirable as noted above.

The non-aqueous solvents employed for leaching the reaction product include such representative solvents as the organic nitriles, alcohols, aldehydes, ketones, toluene, liquid ammonia, amines, liquid sulfur, molten alkali sulfides and polysulfides, carbon bisulfide, nitrobenzene, and pyridines, dimethyl formamide, etc.

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In carrying out the novel process of the instant case, the temperature range for the reduction reaction is maintained in excess of 800° C. and preferably in the range of about 800° C. to 1100° C., such as 1000° C. The reaction pressures are within the range of 1-5 atmospheres.

After the reduction of the titanium sulfides has been effected, the bulk of the alkali sulfide (molten) is drained off at the high temperature and the elemental sulfur, solid, liquid, or vapor, is introduced into the mass for producing polysulfides from the alkali metal sulfides of the reaction product. The reduced titanium therein at the temperatures indicated would not be appreciably affected by the presence of elemental sulfur. The alkali metal polysulfides, which are molten at that low temperature, may now be conveniently drained away from the titanium. Residual polysulfides, or other minor contaminants are finally leached out by non-aqueous (organic) solvents as indicated above. The titanium thus produced is a substantially pure sintered product. Alternately, the reduction product, with or without drainage of molten alkali sulfide, is cooled to temperatures below 300° C. and preferably room temperature and then leached directly with a non-aqueous solvent for the alkali sulfide.

For the purpose of this invention, the starting reactant titanium sulfides may be obtained in many ways, as for example, (1) by heating a mixture of rutile, sodium carbonate, and sulfur; (2) by the vapor phase reaction between titanium tetrachloride and hydrogen sulfide; (3) by the action of hydrogen sulfide on titanium tetrafluoride; and (4) by passing carbon disulfide and hydrogen sulfide over red-hot titanite oxide. It will be apparent that titanium sulfides having a valence of less than 4, namely, TiS, and Ti₂S₃ are also included in the initial titanium sulfides of the present case.

The reduction of titanium sulfides with reducing alkali metals may be effected in several ways as follows:

(1) In a closed chamber at the temperatures and pressures indicated above in the presence of an inert atmosphere. This method is illustrated in Examples 1 and 2.

(2) By a fluidized-bed technique in two steps as illustrated in Example 3.

Example 1

Reduction in a bomb.—Clean sodium metal free of adhering oxide, and anhydrous titanium sulfide are loaded into a stainless steel bomb containing a molybdenum liner and an inert atmosphere of argon. The proportions of these reagents are preferably 47.5 parts by weight of sodium to 52.5 parts by weight of titanium disulfide (10% excess of sodium). After the bomb is closed, it is evacuated and flushed with an inert gas such as argon several times. A final pressure of about one-half an atmosphere is left in the bomb before the reduction is started.

The bomb is best equipped with a sealed thermocouple well so that the reduction can be followed by measuring the temperature of the reacting mass, and also a sealable opening for subsequent addition of sulfur.

Reaction is started by heating the bomb slowly at the rate of 200° C. an hour for about three hours, in a pot furnace. At the end of three hours the temperature of the reacting mass within the bomb rises above the furnace temperature indicating that some reaction is occurring. The heating is continued at the same rate for another hour.

The heat input is cut off after four hours of heating. The temperature within the bomb will continue to rise until it reaches about 1000° C. and then will fall slowly. The furnace and the bomb are allowed to cool below 400° C. Thus cooled, about 135 parts by weight of liquid sulfur is added to the bomb and allowed to stand about an hour at about 300° C. and the sodium polysulfides formed are drained from the bomb and further purged by flushing with argon gas.

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Alternately, the bulk of the sodium sulfide formed as a melt (75-90%) is drained off before cooling from 1000° C. to below 400° C. In this case, only between about $\frac{1}{10}$ and $\frac{1}{4}$ the amount of sulfur is required for the conversion to polysulfide. The contents of the bomb are then allowed to cool to room temperature whereupon the remaining sodium polysulfides are removed by several flushings with alcohol. The remaining titanium when removed from the bomb was found to be substantially pure sintered titanium.

Example 2

Reduction in a bomb.—Clean sodium metal, 39.5 parts by weight, and pure zirconium disulfide, 60.5 parts by weight, are reacted in a bomb following the procedure described in Example 1. The ratio of reactants allows ten percent excess sodium metal over the amount required for stoichiometric considerations. The reaction between zirconium sulfide and sodium metal is more vigorous than that between titanium sulfide and sodium. The reaction began at a furnace temperature of about 600° C., and the temperature of the reacting mass rose to a maximum temperature of about 1100° C. within 30 to 50 minutes, at which time heating was discontinued. The reaction will remain between 1000° C. and 1100° C. for about one-half hour and then fall slowly.

When cooled to about 400° C., 112 parts by weight of liquid sulfur is added to the bomb and allowed to stand about an hour at about 400° C. and the sodium polysulfides formed are drained from the bomb and further purged by flushing with argon gas. The contents of the bomb are then allowed to cool to room temperature whereupon the remaining sodium polysulfides are removed by several flushings with carbon disulfide. The remaining zirconium when removed from the bomb was found to be substantially pure sponge zirconium.

Alternately, the bulk of the sodium sulfide formed as a melt (75-90%) is drained off before cooling from 1000° C. to below 400° C. In this case, only between about $\frac{1}{10}$ and $\frac{1}{4}$ the amount of sulfur is required for the conversion to polysulfide.

Example 3

Reduction in a fluidized column in two steps.—Titanium disulfide is prepared by passing hydrogen sulfide and titanium tetrachloride through a porcelain-lined tube heated to about 500° C. The titanium disulfide is collected as a dust near the exit end of the tube.

The titanium disulfide prepared in this fashion is placed within a fluidization column made from an Alundum tube, and fluidized in a stream of pure hydrogen gas for two hours. The outer wall of the Alundum tube is kept at 1100° C. during this time. The product from the fluidization reaction with hydrogen had an analysis corresponding to 1.2 atoms of sulfur per atom of titanium.

The lower sulfide of titanium produced was then further reduced to the metal titanium by reaction with sodium in the manner indicated in Example 1 above. The reaction was carried out in an inert column of a stainless steel tube having a molybdenum liner and argon gas therein. The walls of the apparatus were kept at about 900° C. during the reduction which required about two hours. The reactants were introduced in the proportions of 42 parts by weight of sodium to 59 parts by weight of the lower titanium sulfide. About 118 parts by weight of sulfur was added to the reduced titanium-sodium sulfide mixture to form the polysulfides of the latter which were separated from the titanium metal by drainage and alcohol solvent extraction in similar manner as indicated in Example 1 above.

It will be evident that various modifications can be made in the process herein disclosed without departing from the spirit of the invention, and it is not my intention to limit the scope of the invention other than necessitated by the scope of appended claims.

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I claim as my invention:

1. The process for producing elemental metals of the group consisting of titanium and zirconium which comprises, reacting the sulfides of said metals with an alkali metal reducing agent at a temperature in excess of 800° C., draining the produced liquid alkali metal sulfides, cooling the mass below 500° C., and adding elemental sulfur thereto to form polysulfides of remaining alkali metals, separating the bulk of the latter from the elemental metal by draining, further cooling to room temperatures and leaching the same with a non-aqueous solvent therefor.

2. The process of claim 1 wherein the reducing agent is selected from the group consisting of sodium and potassium and the reaction temperature is maintained between 800° C. to 1100° C.

3. The process of claim 2 wherein the reducing agent is sodium.

4. The process of claim 2 wherein the reducing agent is potassium.

5. The process of claim 1 wherein the reduction of the metal sulfides is effected in two stages, (1) the partial reduction of the sulfides with hydrogen to the monosulfides and, (2) the final reduction of the monosulfides with sodium.

6. The process of producing metallic titanium which comprises reacting titanium sulfides with an alkali metal reducing agent selected from the group consisting of sodium and potassium at temperatures between 800° C. and 1100° C., cooling the same to a temperature below 300° C., adding sulfur thereto to form polysulfides, and re-

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moving the latter from the titanium by draining and non-aqueous solvent extraction of the remaining polysulfides.

7. The process of claim 6 wherein the reduction reaction is maintained at a temperature of approximately 900° C. in an inert atmosphere.

8. The process of producing elemental titanium which comprises reacting the sulfides of said metal with an alkali metal at elevated temperatures and pressures in an inert atmosphere, partially cooling the same, and adding sulfur to the reaction product, and removing the contaminants of the reaction product by draining and leaching the same with an organic solvent.

9. The process of claim 8 wherein the reduction of the sulfides is effected in two stages, the first being a partial reduction with hydrogen as the reducing agent, and the second being a completion of the reduction with a metal of the group consisting of sodium and potassium.

10. The process of producing elemental zirconium which comprises reacting the sulfides of said metal with an alkali metal at elevated temperatures and pressures in an inert atmosphere, partially cooling the same, adding sulfur to the reaction product, and removing the contaminants of the reaction product by draining and leaching the same with an alcohol.

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